Classification
Physics Abstracts
71.25P — 71.45L

Magnetic properties of κ -(MDTTTF)₂AuI₂ salt in the normal and superconducting states

P. Delhaes ⁽¹⁾, J. Amiell ⁽¹⁾, S. Flandrois ⁽¹⁾, L. Ducasse ⁽²⁾, A. Fritsch ⁽²⁾, B. Hilti ⁽³⁾, C. W. Mayer ⁽³⁾, J. Zambounis ⁽³⁾ and G. C. Papavassiliou ⁽⁴⁾

⁽¹⁾ Centre de Recherche Paul Pascal, CNRS, Château Brivazac, Avenue A. Schweitzer, 33600 Pessac, France

⁽²⁾ Laboratoire de Chimie Théorique, Univ. de Bordeaux I, 33405 Talence, France

⁽³⁾ Central Research Laboratories, Ciba-Geigy AG, 4002 Basel, Switzerland

⁽⁴⁾ Theoretical and Physical Chemistry Institute, National Hellenic Research Foundation, 48 Vassileos Konstantinou, GR 11635 Athens, Greece

(Reçu le 21 décembre 1989, accepté sous forme définitive le 20 février 1990)

Résumé. — Nous avons examiné les propriétés magnétiques (RPE, magnétisme statique et mesures de magnétisation) du nouveau supraconducteur organique κ -(MDTTTF)₂AuI₂ au-dessus et au-dessous de la température de transition sous pression atmosphérique ($T_c \geq 4$ K). La structure électronique de ce sel et de deux composés voisins [κ -(BEDT)₂Cu(SCN)₂ et κ -(BEDT)₂Ag(CN)₂H₂O] a été calculée en employant la méthode de Huckel étendue. L'analyse des résultats expérimentaux et théoriques nous a conduits à proposer une description unifiée indépendante des entités moléculaires présentes. A partir des preuves expérimentales de corrélations électroniques significatives, le problème de la compétition entre les états à basse température AF et SC a été examiné. Cependant, en l'absence d'aucune évidence expérimentale d'un état AF, l'origine des paires d'électrons n'est pas éclaircie dans ces matériaux quasiment bidimensionnels.

Abstract. — We have investigated the magnetic properties (ESR, static susceptibility and magnetization experiments) of the new organic superconductor κ -(MDTTTF)₂AuI₂ above and below the SC phase transition temperature ($T_c \geq 4$ K). At ambient pressure the electronic structures of this salt and of two related compounds [κ -(BEDT)₂Cu(SCN)₂ and κ -(BEDT)₂Ag(CN)₂, H₂O] have been calculated using an extended Huckel method. The analysis of both experimental results and calculated data has led us to propose a unified picture independently of the present molecular blocks. Finally the problem of the competition between the SC and AF low-temperature states which is based on the experimental evidences of electronic correlations has been examined. However, in the absence of any experimental evidence of an AF state, the origin of the electron pairing is still unclear in these quasi 2d materials.

Introduction.

The list of organic and metallo-organic molecules which give superconducting radical-ion salts (RIS) is steadily expanding [1]. After the initial discoveries with TMTSF (tetramethyltet-

raselenafulvalene) and BEDT (bisethylenedithiotetrathiafulvalene) symmetrical donor molecules it has recently been evidenced that unsymmetrical ones, such as DMET (a « hybrid » between the first two molecules) and MDTTTF (methylenedithiotetrathiafulvalene), [2], are also ambient pressure superconductors. A characteristic feature of BEDT is its propensity to give salts in several crystal morphologies (α , β , γ , θ , κ , ... forms) with, in particular, a $\kappa(\text{BEDT})_2\text{-Cu}(\text{SCN})_2$ salt which exhibits the highest superconducting (SC) transition actually known ($T_c \approx 10.5$ K) [1]. The recent discovery of $(\text{MDTTTF})_2\text{AuI}_2$ as a new molecular superconductor ($T_c \approx 4$ K) is noteworthy because of its similarity of donor packing with this BEDT salt. In both cases we are in the presence of radical-cation dimers which are orthogonally arranged to form a 2d structural network and therefore to give rise to an anisotropic 2d electronic system. We have investigated the magnetic properties of this new compound for, on the one hand, fully characterizing the SC state, and on the other hand, looking for a possible competing antiferromagnetic (AF) state. Finally, we will explain the experimental results by comparison with the other known κ -type compounds: $\text{Cu}(\text{SCN})_2$ ($T_c = 10.5$ K), I_3 ($T_c = 3.5$ K), [3] $\text{Hg}_{2.89}\text{Br}_8$ ($T_c = 4.3$ K), [4], and $\text{Ag}(\text{CN})_2$ (no apparent SC state) [5] BEDT salts but also $(\text{DMET})_2\text{AuBr}_2$ ($T_c = 1.9$ K), [6]. All these compounds constitute a homeomorphic group with common physical features that we will discuss.

Experimental.

The MDT-TTF molecule (see insert of Fig. 1) has been synthesized following a procedure described previously [2]. Crystals of $\kappa(\text{MDTTTF})_2\text{AuI}_2$ were grown by the classical electro-oxidation technique at constant current ($I \approx 1\text{-}2 \mu\text{A}$) in THF as a solvent and with $(\text{nBu})_4\text{NAuI}_2$ as the supporting electrolyte: small black platelets were obtained which

Fig. 1. — The temperature dependence of the paramagnetic susceptibility (full line) measured on a polycrystalline sample of $(\text{MDTTTF})_2\text{AuI}_2$ (see insert for the chemical formula) with the Faraday balance and the Pauli type susceptibility (dotted line) calculated from the density of states at the Fermi level $N(E_F)$.

crystallize in the orthorhombic system (space group P_{bmn}). The centrosymmetric dimers lie in the ab plane ; along the c -axis these sheets are separated by AuI_2 planes.

These crystals exhibit a moderate room temperature electrical conductivity with a metallic type dependence below 200 K, [2]. ESR experiments on single crystals were carried out with an X (and Q) band Varian spectrometer equipped with an Oxford variable temperature accessory. Measurements of static susceptibility on a polycrystalline batch (15 mg) were performed with a standard Faraday balance between 4 and 290 K in the presence of a magnetic field strength of 1.1 T. Besides, for the low temperature data (1.8-15 K), we have used a SQUID magnetometer (SHE company) working with a variable magnetic field strength (0 to 60 kOe).

Results.

MAGNETISM IN THE NORMAL STATE. — The static susceptibility measured with the Faraday balance was corrected for the core diamagnetic component calculated, as usual, from Pascal's constants. We neglect a possible presence of a small Landau-type diamagnetism. The temperature dependence of the paramagnetic susceptibility is shown in figure 1. A weak temperature dependence, more or less characteristic of Pauli paramagnetism, is observed with a flat maximum followed by a small minimum around 20 K ; besides, the extrapolated absolute value $(\chi_p)_0 \sim 6 \times 10^{-4}$ emu. CGS mole $^{-1}$ is quite high, as in most of the TTF type radical-cation salts, indicating the presence of strong electronic correlations (see next part).

ESR experiments give the g -value and linewidth room temperature anisotropy by exploring their angular dependences on single crystals. As indicated in figure 2, we detect a weak anisotropy for both line position and width characteristics which correspond to a Lorentzian absorption curve, except in the case when the platelet is horizontal (the c axis aligned with the static magnetic field) where a weakly Dysonian line is observed.

For this orthorhombic crystal [2], after checking that the principal axes of these second rank tensors are aligned with the crystallographic axis, we confirm the correspondence between the extrema values of the linewidth and the g -factor values, [7]. It is well known that the principal values of the g -factor are molecular characteristics more or less constant in the TTF series ($g_1 \geq 2.010$, $g_2 \approx 2.007$, $g_3 \approx 2.003$ respectively along the directions of the molecular long axis, short axis and normal to the molecular planes) [8]. In the present case, we rather observe mean values because of the presence of more or less orthogonalized dimers ; as evidenced by the crystal structure [2], the two a and b crystallographic directions are almost equivalent and the ESR signal appears to present an axial symmetry. This point is confirmed by the tensor trace which has to be invariant for these radical-cation species ($\langle g \rangle \approx 2.0063$).

Concerning the linewidth ΔH which is almost isotropic, we have been looking for a frequency dependence by using a room temperature Q -band spectrometer : a constant linewidth has been observed. Therefore there is no apparent frequency dependent exchange effect at 290 K in this compound as found in classical magnetic insulators.

The temperature dependences of both the linewidth and the line position for a given crystal orientation ($H_0 // a$) are given in figure 2. The g -factor is temperature independent while the linewidth is increasing when the temperature is decreased, almost linearly down to 100 K and with a strong regime change around $T^* \approx 70$ K. Finally, after a broadening the resonance line is lost around 50 K and a new line is observed below 20 K which does not behave as a classical AF resonance line. Its characteristics are independent of the magnetic field direction : $g \approx 2.060$, $\Delta H \approx 90$ gauss with an estimated intensity about one per cent of the intrinsic line. This is an extrinsic effect which could be associated with the tri-iodide of MDTTTF prepared as an impurity during the crystallization process.

Fig. 2. — The temperature dependences of the ESR g -factor and linewidth (ΔH) for a given crystal orientation ($\vec{H}_0 // \vec{a}$) of the $(\text{MDTTTF})_2\text{AuI}_2$ compound. The g -factor and linewidth (ΔH) room temperature principal values are also given. (In the insert, the normalized resistance T dependence published previously [2]).

Nevertheless, the intrinsic behavior is the linewidth linear increase between 300 and 60 K ; this is in contrast with the classical temperature decrease in RIS which are one-chain compounds. This result has also been observed in other κ salts, [1, 4, 9]. As we will explain in the next part, this effect is associated with the intermediate values observed for these g -factor components because they result from the back and forth spin motion between the two kinds of dimers.

MAGNETISM IN THE SUPERCONDUCTING STATE. — Magnetization measurements on powder samples have been carried out at ambient pressure *versus* magnetic field (H) and temperature (T) (Fig. 3). These results allow us to confirm that we are in the presence of a bulk

Fig. 3. — Magnetic field dependences of the magnetization at different temperatures (in the insert, the temperature dependences exhibiting the diamagnetic shielding and Meissner effects under a weak magnetic field).

superconductor with a transition temperature $T_c \approx 4 \text{ K}$. These magnetic field isothermal dependences have demonstrated that :

— at $T > T_c$ there is no apparent antiferromagnetic state, which could be detected by AF resonance, the anisotropy of the static susceptibility, or even by the analysis of d.c. electrical conductivity T -dependence (see insert of Fig. 2) [10].

— at $T < T_c$ there is a diamagnetic state as predicted by the classical SC theory (the bump observed around 2 K should be due to the anisotropic effects present in these layered structure type superconductors).

To confirm this observation of a diamagnetic ground state, we have carried out the temperature dependences in the presence of a low magnetic field strength (see insert of Fig. 3). The sample is first cooled in the absence of any magnetic field down to 1.8 K, then the field is applied and the magnetization is measured upon heating : the diamagnetic shielding is observed. When the sample is subsequently cooled under magnetic field the Meissner effect is also detected.

Our observations are very similar to those already reported on organic SC [11, 12]. From the saturation value of the Meissner effect when the temperature is going down to zero Kelvin, we calculate the effective fraction of complete diamagnetism $M_{\text{Meiss}} \approx 7\% M_{\text{dia}}$ a rather low value, nevertheless quite usual in these materials [12]. The measurement of M - H static hysteresis loop has been performed at 1.6 K (Fig. 4). This experiment allows us to estimate the critical current density $I_c \propto \frac{\Delta M}{D}$ as predicted by Bean's model [13], where ΔM is the difference in magnetization at a fixed value for increasing and decreasing fields, and D is the mean grain diameter. Estimating $D \approx 10^{-4}$ m and $H \approx 500$ Oersted we obtain a quite low but acceptable value $I_c \approx 3\,700$ A/cm².

The last piece of information provided by this experiment is about the derivation of the lower critical field H_{c1} which is defined as the field where the flux starts to penetrate into the sample and thus corresponds to the first deviation from linearity in the magnetization curve : the apparent mean value is $\bar{H}_{c1} \approx 50$ Oersted, a rather high figure (see Fig. 4).

Fig. 4. — M . H . Hysteresis loop at constant temperature ($T = 1.6$ K) obtained with a succession of steady states.

From the magnetic field dependence observed at 2 K (Fig. 3), we can also estimate the upper critical field value $\bar{H}_{c2} \approx 15$ kOersted which is in rough agreement with the estimated Pauli limit. These results are similar to those observed on β and κ -phases superconductors, [1, 12]. These compounds are anisotropic type II SC, well described by the Ginzburg-Landau theory; however to apply this theory it will be necessary to work on single crystals, [14]. Actually, with the present results only mean approximate values for the critical fields are given, and they do not allow us to give a valuable estimate of the coherent lengths.

ELECTRONIC STRUCTURE OF κ -(MDTTTF) $_2$ AuI $_2$ AND RELATED COMPOUNDS.

The electronic structure of the title compound is compared to the band structure characteristics of two other κ -type salts, namely κ -(BEDT) $_2$ Cu(SCN) $_2$ and κ -(BEDT) $_2$ Ag(CN) $_2$ H $_2$ O. Tight-binding calculations based upon the Extended Hückel theory have been performed. For κ -(BEDT) $_2$ Cu(SCN) $_2$ and κ -(BEDT) $_2$ Ag(CN) $_2$ H $_2$ O, these structures have already been determined [1, 5]. As some technical differences may be found between the authors (simple vs double basis set, values of the parameters), in this paper we compare the results obtained within the same approximations.

The transfer integrals are evaluated within the dimer splitting approximation [15]; they involve the coupling between the HOMO (highest occupied molecular orbital) of each organic molecule. For parallel molecules, the transfer integrals couple p_z atomic orbitals (AO) located on each monomer while p_z AO on one more monomer and p_y AO on the other monomer are coupled through the transfer integrals between perpendicular molecules (see Fig. 5, for the transfer integral labelling and the definition of the reference axes). The transfer integral values are given in table I: the symmetry groups of this AuI $_2$ salt on the one hand, and the BEDT compounds on the other hand are different and this explains that the number of equivalent transfer integrals is reduced in the former case.

Fig. 5. — Projection of the κ structure in the (b, x) plane (x is the a axis for Au and Ag salts and the c axis for Cu) giving the transfer integral labelling.

The transfer integrals are comparable, especially those relative to the BEDT salts. The MDTTTF salt exhibits a smaller dimerization parameter S_1/S_2 . The BEDT different molecular symmetry does not lead to qualitative differences (compare t_{I1} and t_{I3} , t_{I2} and t_{I4}). The resulting band structures are similar to those given previously so that only the Fermi surfaces are shown in figure 6. A slight difference is noted at the Brillouin zone

Table I. — *Transfer integrals expressed in meV.*

t (meV)	$(\text{MDTTTF})_2\text{AuI}_2$	$(\text{BEDT})_2\text{Ag}(\text{CN})_2\text{H}_2\text{O}$	$(\text{BEDT})_2\text{Cu}(\text{SCN})_2$
S1	150.3	136.1	135.5
S2	106.0	35.3	50.2
I1	15.1	46.2	47.6
I2	45.2	31.5	27.6
I3	15.1	50.8	41.4
I4	45.2	23.2	30.9

Fig. 6. — Fermi surfaces of the κ -phase salts.

boundaries, where the contact of the two circular surfaces (which is observed in MDTTTF salt) is not allowed in the two BEDT salts by their lower crystal symmetry.

The density of states was calculated and is shown for the three salts in figure 7. The results evidence that there exist two Van Hove-like singularities. The larger one, which is found at the lower energy for MDTTTF and below the Fermi position for the BEDT salts corresponds to a flat band around the center of the Brillouin zone. The second singularity corresponds to a small dispersion along the M - Y direction. The density of states at the Fermi level for these

Fig. 7. — Density of states $N(E)$ versus energy (E) of the two upper bands for the three considered κ -salts. (Note the energy range slightly different for the three salts).

Table II. — *Summary of physical properties for three κ -phase compounds.*

κ salts	Electronic band parameters			Experimental characteristics			
	$N(E_F)$	$\left(\frac{\langle t_{\perp} \rangle}{\langle t_{\parallel} \rangle}\right)$	bandwidth Δ (eV) and Fermi level E_F (eV)	$\chi_{\text{exp}} 10^4$	Enhancement factor	ESR linewidth regime change	SC state T_c (K)
	($\text{eV}^{-1} \text{ mol}$)			(emu. cgs mole $^{-1}$) ($\chi_{\text{exp}}/\chi_{\text{Pauli}}$)		T^* (K)	
(BEDT) $_2$ Cu(SCN) $_2$ [1]	7.3	0.46	0.300 0.128	4.6	2.0	20	10.4
(BEDT) $_2$ Ag(CN) $_2$, H $_2$ O [5]	8.3	0.53	0.303 0.131	4.6	2.0	55 —	—
(MDTTTF) $_2$ AuI $_2$	7.0	0.29	0.340 0.158	6.2	2.6	70	4

half-filled band systems, $N(E_F)$ is given in table II: it is quite similar for the three compounds. It has to be noticed that $N(E_F)$ does not lie in the region of the singularity of density of states but rather on the upper wing. Moreover, if one assumes that the transfer integrals might increase at low temperatures it is found that E_F will shift to a higher position while the singularities will stand more or less at the same energy, thus implying a decrease of $N(E_F)$.

Interpretation and comments.

We will focus our discussion on three related points: the enhanced paramagnetic state, the ESR linewidth T -dependence and the occurrence of the SC state. In order to introduce these comments we have summarized in table II the electron band parameters and the main experimental characteristics for the MDTTTF compound and also for the other two BEDT salts which have been carefully investigated.

The quasi 2d electronic structure may be modelled by two transfer integrals: one denoted $\langle t_{\parallel} \rangle$ is an average of the interactions between parallel dimers while the other $\langle t_{\perp} \rangle$ involves perpendicular molecules (see Fig. 5). This simple model allows us to evaluate the effective electronic anisotropy $\frac{\langle t_{\perp} \rangle}{\langle t_{\parallel} \rangle}$ as shown in table II. The 2d electronic character increases from

MDTTTF to BEDT salts as a consequence of a smaller dimerisation parameter $\left(\frac{t_{S_1}}{t_{S_2}}\right)$ and a weaker t_{I_1} in the former case; however in every case we are in the presence of quite narrow electronic bands (the total bandwidth is about $\Delta \simeq 0.30 - 0.34$ eV).

PARAMAGNETIC STATE AND EVIDENCE FOR ELECTRONIC CORRELATIONS. — From the comparison between the quasi constant experimental paramagnetism and the calculated Pauli paramagnetism ($\chi_{\text{Pauli}} \propto N(E_F)$) we calculate the enhancement factor (see Fig. 1 and Tab. II), which is 2.6 for the present compound and around 2.0 for the corresponding BEDT salts. As currently admitted [16] this is due to the electronic correlations which are evidenced by the presence of charge transfer bands in optical absorption spectroscopy [17]. Indeed a preliminary experiment has shown that we observe two intense C. T. bands around 3 400 and 12 500 cm^{-1} as in BEDT salts [18]. These band frequencies are related to the on-site (U) and

first neighbor site (V) Coulomb interactions in the atomic limit of the extended Hubbard model, an approximation which overestimates U and V [17]. These parameters, which are essentially molecular characteristics, are estimated to be about 1-1.2 eV and 0.4 eV respectively in these compounds. If we compare with the calculated bandwidth (Tab. II) we conclude that $\Delta \simeq V < U$ i.e. the electronic correlations should be dominant in these narrow electronic band systems even if, up to now, we have not been able to detect any apparent AF state near the present SC state.

ESR LINEWIDTH T-DEPENDENCE. — This behavior has been the subject of a long controversy in quasi 1d organic conductors because no firm theory really exists.

Two main problems are present : on the one hand, the relaxation mechanism and therefore the linewidth value which are functions of the electronic dimensionality, and, on the other hand, their temperature dependences, either an increase or a decrease of the linewidth is observed with the temperature decrease.

Based upon the experimental facts a general rule can be established which suffers very scarce exceptions :

i) For radical ion salts, or one-chain compounds, the linewidths are decreasing with temperature.

ii) For charge transfer complexes such as TTF-TCNQ, or two-chain compounds, the linewidths are generally increasing when the experimental temperature is going down in the absence of any phase transition [19].

The first situation is classical and reminiscent of a mechanism for the spin-relaxation process through the lattice scattering and the associated motional narrowing effect which is present in classical 3d metals [20].

It has been demonstrated by Elliott [21] and Yafet [22] that the linewidth and the g -factor values are proportional to the spin-orbit coupling ; these two quantities are related by Elliott's relation :

$$\Delta H \propto \frac{(\Delta g)^2}{\tau_{e-ph}} \tag{1}$$

where Δg is the g -factor anisotropy and τ_{e-ph} is the usual electrical conductivity relaxation time ; it follows that in a metallic state ΔH and the electrical resistivity must follow a similar T -dependence. As pointed out by Tomkiewicz *et al.* [23] in an ideal 1d electronic system this relaxation mechanism cannot exist. This is the reason why the observed linewidths are several orders of magnitude lower than the expected ones.

In partial 2d conductors where transverse electronic interactions are present, the dimensionality change is empirically accounted for by a correcting factor $\left(\frac{t_{\perp}}{t_{\parallel}}\right)^2$ which allows us to explain the linewidth broadening and the similar T -dependence characteristic of one chain compounds [26].

In order to explain the opposite behavior observed in TTF-TCNQ and related compounds Weger has proposed the following argument [25] : the measure of the 2d character is determined by the ratio $\left(\frac{\tau_{\parallel}}{\tau_{\perp}}\right)$ where $\tau_{\parallel}$ (with $\tau_{e-ph} \equiv \tau_{\parallel}$) is the on-chain scattering time and $\tau_{\perp}$ is the transverse tunneling time ;

$$\Delta H \propto \frac{(\Delta g)^2}{\tau_{\perp}} . \tag{2}$$

In the case where the longitudinal conductivity is coherent (this is the case for these compounds at least below room temperature) and the transverse conductivity is diffusive, Weger has shown that the probability for hopping between neighboring chain is :

$$\tau_{\perp}^{-1} = \frac{1}{\hbar^2} |t_{\perp}|^2 \tau_{\parallel} . \quad (3)$$

This derivation assumes that the two chains (or dimers) are degenerate in energy (but their ESR signal can present a different g -factor). The application of (3) modifies the Elliott-Weger relation (2) :

$$\Delta H \propto (\Delta g)^2 |t_{\perp}|^2 \tau_{e-ph} . \quad (4)$$

In this situation the linewidth increases with $t_{\perp}$ value and the associated electronic dimensionality, but also follows the electrical conductivity temperature dependence (indeed a coexistence of the two mechanisms can also be empirically considered in order to fit every experimental situation [24]).

This approach is in favor of our and other experimental observations on κ -salts :

- The linewidths for the κ -phases ($\Delta H \simeq 60 - 100$ gauss at 290 K) are in general larger than for the other phases which are more 1d type compounds ($\Delta H = 10 - 20$ gauss) [8].
- They are linearly increasing between room temperature and T^* where a regime change occurs (see Tab. II).

This is only in qualitative agreement with the electrical conductivity T -dependence which appears to be rather complex in this MDTTTF salt (see insert of Fig. 2) ; however it shows that Weger's argument can be extended to these quasi 2d electronic systems.

It appears equivalent to be in the presence of one kind of donors (or acceptors) presenting two different crystallographic positions in the lattice or to have both donor and acceptor molecules in charge transfer complexes.

Besides, the presence of a sharp regime change in the linewidth T -dependence means that around T^* the spin relaxation mechanisms are strongly modified. As already discussed, the linewidth broadening could be attributed to the onset of an AF state but in the absence of any other experimental evidence, this hypothesis cannot be maintained.

Other possible suggestions to explain this general behavior are either a diffuse to coherent transition of one component of the transverse electrical conductivity [25] occurring in these salts or even a structural change.

OCCURRENCE OF A SUPERCONDUCTING STATE. — κ -(MDTTTF)₂AuI₂ is an anisotropic type II superconductor like the other β and κ superconducting BEDT salts.

The main experimental fact is that all these κ -phase compounds are low temperature superconductors except one of them : (BEDT)₂Ag(CN)₂H₂O [5]. Nevertheless for technical reasons the low temperature electrical conductivity has not been completely investigated [27], but we can guess that the SC state should be present (if some disorder effect associated with the presence of molecules of water does not suppress it).

It is necessary therefore to look for a general origin, whatever the molecular characteristics of the symmetrical or unsymmetrical molecules involved.

In a recent review the alternative ways for the mechanisms of superconductivity in layered structures have been carefully examined by Friedel [28] and some arguments used for the perovskite high T_c superconductors can be invoked.

As in copper oxides [29] the presence of large Van Hove anomalies in the density of states near the Fermi level resulting from the two-dimensional character is a possible mechanism.

But it turns out that in the present electronic situation $\left(\frac{\langle t_{\perp} \rangle}{\langle t_{\parallel} \rangle} < 1 \right)$ our energy band calculation (Fig. 7) does not exhibit this coincidence; we have found that $N(E_F)$ is quite constant in this series of salts (Tab. II) and almost identical to the values also proposed for the β phase BEDT superconductors [1]. The different T_c values which have been observed are therefore due to a change in the pairing coupling mechanism which is subject to discussions in these materials [28].

It has been proposed, for the first series of organic SC, namely the TMTSF salts, that the origin of the BCS type coupling mechanism is the electron-electron repulsion *via* the antiferromagnetic fluctuations which are present in these quasi 1d materials [30]. Indeed, for a given stoichiometric phase in a thermodynamic phase diagram, both SC and AF states have been observed, which are connected and mutually exclusive.

In the present series of compounds which are anisotropic 2d electronic systems (the Fermi surfaces presented in Fig. 6 are almost closed) we have observed the presence of sizeable electron-electron correlations on the one hand, but no experimental evidence of an AF state on the other hand. This is a crucial point which has to be elucidated, because theoretical 2d Hubbard models show that the competition between AF and SC states [31] is in favour of the SC state for a half-filled band. Even a recent study [32] claim the possibility of superconductivity without the proximity of an AF state. One experimental way to answer this question would be to play with the band filling factor as in high T_c superconductors which is fixed by the (2-1) salt stoichiometry in all these organic conductors.

Conclusion.

We have investigated the magnetic properties of κ -(MDTTTF)₂AuI₂ in the normal and the SC states. We have shown in the high temperature phase the presence of rather strong electronic interactions in these narrow band compounds. The ESR linewidth T -dependence, which does not obey the usual Elliott relation, has been explained using an argument already proposed by Weger [25] for the two-chain compounds i.e. charge transfer complexes (TTF-TCNQ type). Besides we have pointed out that the sudden broadening of this linewidth around T^* is an intrinsic behavior for this class of compounds.

We have also confirmed that this compound is a volume second kind superconductor below 4 K and more generally that almost all the κ -phase compounds present a similar behavior. A unified picture of these salts has been tentatively developed based upon the magnetic properties and the electronic band calculations which unfortunately do not take the electronic interactions into account. For a general description of the physics of anisotropic 2d electronic systems we have examined the possible competition between SC and AF states but we have no evidence of even a hidden AF state. The origin of the electron pairing, in these materials, remains therefore subject to controversy.

Acknowledgements.

We thank Dr. M. Kurmoo for the κ -(BEDT)₂Ag(CN)₂, H₂O crystal data and an interesting discussion, Dr. M. Kinoshita for the κ -(BEDT)₂Cu(SCN)₂ crystal data, and Mrs. B. Agricole for helpful technical assistance.

Note added in proof:

In a very recent publication the structural and electronic properties of the κ -phase organic conductors have also been discussed in order to understand the occurrence of the superconducting state (D. Jung *et al.*, *Inorg. Chem.* **28**, p. 4516, 1989).

References

- [1] SAITO G., in *Advances in superconductivity*, p. 107, Kitawaza-Ishiguro Eds. (Springer Verlag, Tokyo, 1989) and publications therein.
- [2] PAPAVALASSIOU G. C., MOUSDIS G. A., ZAMBOUNIS J. S., TERZIS A., HOUNTAS A., HILTI B., MAYER C.W. and PFEIFFER (J.), *Synth. Met.* **27B** (1988) 379.
- [3] KOBAYASHI A., KATO R., MORIYAMA H., NISHIO Y., KAJITA K. and SASAKI W., *Chem. Lett.* (1987) p. 459.
- [4] LUBOVSKAYA R. N., ZHILYAEVA E. I., PESOZKY S. I., *Pisma Zh. Elesp. Teor. Fiz.* **46** (1987) p. 149.
- [5] KURMOO M., TALHAM D. R. and DAY P., To appear in NATO ASI series « Lower dimensional systems and molecular electronics », R. M. Metzger Ed.
- [6] KIKUCHI K., HONDA Y., ISHIKAWA Y., SAITO K., IKEMOTO I., MURATA K., ANZAI H., ISHIGURO T. and KOBAMASUI K., *Sol. Stat. Commun.* **66** (1988) 405.
- [7] SUGANO T., SAITO G. and KINOSHITA M., *Phys. Rev. B* **34** (1986) 117.
- [8] ENOKI T., IMAEDA K., KOBAYASHI M., INOKUCHI H. and SAITO G., *Phys. Rev. B* **33** (1986) 1553.
- [9] SEKRETARCZYK G., GRAJA A. and LYUBOVSKAYA R. N., *Mater. Sci.* **XIV** (1989) 59.
- [10] COULON C., in *Organic and Inorganic low-dimensional crystalline materials*, p. 201, NATO ASI B168, P. Delhaes and M. Drillon Eds. (Plenum Press, 1987).
- [11] HEIDMANN C. P., VEITH H., ANDRES K., FUCHS H., POLBORN K. and AMBERGER E., *Sol. State Commun.* **57** (1982) 161.
- [12] SCHWENK H., PARKIN S. S. P., LEE V. Y. and GREENE R. L., *Phys. Rev. B* **34** (1986) 3156.
- [13] BEAN C. P., *Phys. Rev. Lett.* **8** (1962) 250.
- [14] FREUND M. M., HILTI B., MAYER C. W. and ZAMBOUNIS J. S. (to be published).
- [15] DUCASSE L., ABDERRABBA M., HOARAU J., PESQUER M., GALLOIS B. and GAULTIER J., *J. Phys. C* **19** (1986) 3805.
- [16] TORRANCE J. B. in *Chemistry and Physics of 1d Metals*, p. 137, NATO ASI B25 H. J. Keller Ed. (Plenum Press, 1977).
- [17] DELHAES P. and GARRIGOU-LAGRANGE C., *Phase transit.* **13** (1988) 87.
- [18] GARRIGOU-LAGRANGE C. (Private communication).
- [19] DELHAES P., KERYER G., GAULTIER J., FABRE J. M. and GIRAL L., *J. Chim. Phys.* **79** (1982) 299.
- [20] MONOD P. and BEUNEU F., *Phys. Rev. B* **19** (1979) 911.
- [21] ELLIOTT R. J., *Phys. Rev.* **96** (1954) 266.
- [22] YAFET Y., *Solid State Phys.* **14** (1963) 1.
- [23] TOMKIEWICZ Y., ENGLER E. M. and SCHULTZ T. D., *Phys. Rev. Lett.* **35** (1975) 456.
- [24] BLOCH A. N., CARRUTHERS T. F., POEHLER T. D. and COWAN D. D., in NATO ASI B25, J. H. Keller Ed. (Plenum Press) 1977.
- [25] WEGER M., *J. Phys. France Colloq.* **39** (1978) C6-1456.
- [26] SANQUER M., BOUFFARD S. and FORRO L., *J. Phys. France* **47** (1986) 1035.
- [27] KURMOO M. (Private communication).
- [28] FRIEDEL G., *J. Phys. Condens. Matter* **1** (1989) 7757.
- [29] LABBE J. and BOK J., *Europhys. Lett.* **3** (1987) 1225.
- [30] JEROME D., CREUZET F. and BOURBONNAIS C., *Phys. Scripta* **27** (1989) 130.
- [31] LEDERER P., MONTAMBAUX G. and POILBLANC D., *J. Phys. France* **48** (1987) 1613.
- [32] MAZUMDAR S., *Solid State Commun.* **66** (1988) 427.